



Physicochemical and phytochemical characterization of green coffee, cinnamon clove, and nutmeg EEGO, and aroma evaluation of the raw powders

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Abstract

The aim of the present study was to estimate the antioxidant activity, total phenolic, caffeic acid and quercetin contents, along with color parameters and pH of green coffee, cinnamon clove and nutmeg powders using their ethanolic extracts of grape origin (EEGO). In addition, volatile compounds' analysis was done using solid phase dynamic extraction coupled to gas chromatography mass spectrometry (SPDE/GC–MS) to the raw powders. Results showed that the highest average antioxidant activity (59.62%), total phenolic content (1160.49 mg GAE/L), and caffeic acid content (1978.20 mg/L) had green coffee EEGO. The respective values for cinnamon clove EEGO were: 55.12%, 1120.24 mg GAE/L, and 634.66 mg/L, whereas those of nutmeg EEGO were: 57.24%, 199.39 mg GAE/L, and 30.43 mg/L. Quercetin had the highest content in cinnamon clove (566.77 mg/L), followed by green coffee (141.75 mg/L), and nutmeg 18.24 (mg/L) EEGO, respectively. Color parameters and pH differed significantly ($p < 0.05$) among the studied EEGO. Volatile compounds (alcohols, aldehydes, esters, ketones, phenolic compounds, etc.) differed significantly ($p < 0.05$) among the studied powders. The present findings confirm that ethanol of grape origin can be used as an edible and eco-friendly solvent to extract the phytochemicals found in green coffee, cinnamon clove, and nutmeg powders (which also possess a characteristic aroma), providing additional knowledge, on the potential use of these extracts as natural food preservatives. Ongoing research will further approve this hypothesis.

Keywords Phytochemicals: EEGO · Green coffee · Cinnamon clove · Nutmeg · Volatile compounds

Introduction

Since 1500 BC, ancient Egyptians used different spices for food preservation and flavoring. During the Middle Ages, herbs and spices were used also for flavoring, food preservation and medicinal purposes, to treat infectious diseases and cholera (Raghavan, 2006) [1]. A considerable number of studies attributed their antioxidant, antimicrobial and pharmaceutical properties to their complex mixture of phenolic compounds such as terpenoids and flavonoid [2]. Spices are sources of polyphenolic compounds that have strong antioxidant capacities and could add additional health benefits [3]. Different spices can be used in foods to help inhibiting

the free radicals formed in the human body, by factors such as heat, radiation, UV light and tobacco smoke. Cinnamon is obtained from the inner bark of different trees of genus *Cinnamomum* and belongs to the Lauraceae family. There are about 250 known species of genus *Cinnamomum* with the most common, *Cinnamomum verum* (Ceylon Cinnamon), *Cinnamomum cassia* (Saigon Cinnamon), *Cinnamomum burmannii* (Korintje Cinnamon), and *Cinnamomum loureiroi* (Royal Cinnamon). Cinnamon Lauraceae spices contain eugenol, but the strong antioxidant activity is attributed to its high cinnamaldehyde content in addition to eugenol [3]. Also, it contains bioactive compounds that have protective properties against diabetes, obesity, hypertension and hypercholesterolemia [4]. Bacanlı et al. [5] reported that coffee and cinnamon contain cinnamic acid which has antioxidant, antihyperglycemic and ameliorative effects on diabetic complications. Cloves are the flower buds of a tree that belongs to the family of Myrtaceae, *Syzygium aromaticum*, and is a commonly used as a spice, flavoring, medical properties, but also cosmetics. Indonesia, India, Madagascar, and Pakistan

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are the countries that clove is produced and is exported in huge amounts. Clove contains a number of bioactive compounds such as flavonoids, hydroxycinnamic acids, hydroxybenzoic acids and others, but the major phenolic constituent in cloves is eugenol, which contributes to its high antioxidant activity [6]. Nutmeg (*Myristica fragrans*), is a leafy evergreen tree that belongs to family Myristicaceae, a family of flowering plants that can be found in Asia, Africa, Pacific islands, and America [7, 8]. *Myristica fragrans* is the source of nutmeg and mace spices, its genus is consisted by 150 species that are spread in Western Pacific and Asia. It was discovered by Portuguese at 1512 in Indonesia. Nutmeg consists mainly of lipids (30–40%) and essential oils (10%). The distinctive odor of nutmeg is due to the essential oil which contains terpenes, terpene derivatives and phenylpropanes. Nutmeg's antioxidant activity is due to the of various compounds that includes, such as β -caryophyllene and eugenol. These compounds have their hydrogen atoms in the allylic or benzylic positions and cause of the comparatively simple abstraction of atomic hydrogen from these functional groups, these compounds have high antioxidant activity [7]. Previous studies showed that nutmeg has aphrodisiac, hypolipidemic, antithrombotic, antifungal, antidysentery, stomachic, carminative, tonic, nerve stimulant, aromatic, narcotic, astringent, hypolipidemic, antithrombotic, antifungal, antidysentery, and anti-inflammatory properties. It has been also reported that helps in paralysis and improves blood circulation [9]. Coffee is one of the most valuable and important beverage for the global economy [10]. The main species production is Arabica coffee (*Coffea arabica* L.) with a share of 64.5% [11] and Brazil is the world's largest producer. After harvesting, coffee cherries are peeled off and coffee beans are dried by the sun, before being roasted. During the roasting progress, compounds that are responsible for its aroma are produced through the Maillard reaction, pyrolysis, and degradation. However, some volatile compounds that are contained at green beans, are lost or change to other forms due to the Maillard reaction, as a result, coffee beans show greater antioxidant activity before roasting due to their huge amount of polyphenols [12]. Chlorogenic acid like caffeic-acid are the most prevalent phenolic compounds of coffee [13], and it is responsible for coffee pigmentation, astringency, aroma formation and acidity to coffee brew [12].

The antioxidant activity of the above natural food sources is estimated using spectrophotometric assays, such as 2,2-diphenyl-1-picryl-hydrazyl (DPPH) [11], ferric reducing antioxidant properties (FRAP), 2,2'-azinobis(3-ethylbenzothiaziline-6-sulfonate) (ABTS), microsomal lipid peroxidation (MLP), etc. [3]. On the other hand, the aroma of these matrices is determined using gas chromatography (GC) alone or in combination with mass spectrometry (GC-MS) [14], solid phase microextraction coupled to gas

chromatography/mass spectrometry [15], and more recently, using proton transfer reaction-time of flight mass spectrometry (PTR-TOFMS) [16].

In addition, the previous years and in recent times the synthetic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tert-butylated hydroquinone (TBHQ), propyl gallate (PG) and octyl gallate (OG) have been used extensively to inhibit the oxidation in foods. However, the most recent epidemiological studies have pointed to the possible health risks associated with the consumption of synthetic antioxidants in foods [3].

Based on the above, the aim of the present study was to estimate the antioxidant activity, total phenolic, caffeic acid and quercetin contents, along with color parameters and pH of green coffee, cinnamon clove and nutmeg powders using their ethanolic extracts of grape origin (EEGO) (ethanol obtained through distillation of dry white wine). Complementary analysis included the determination of aroma compounds of the raw powders, using solid phase dynamic extraction coupled to gas chromatography mass/spectrometry (SPDE-GC/MS). To the best of our knowledge, there is scarce data in the literature on the content and determination of phytochemicals using "a green" and "eco-friendly" solvent, and on the general concept of the present study with insights into the potential use of EEGO, in the near future, for food preservation, this constituting the novelty of the present study.

Materials and methods

Preparation of green coffee, cinnamon clove, and nutmeg powders

Green coffee (*Coffea arabica*, Guatemala Jasmin SHB EP), cinnamon (*Cinnamomum burmanni*, Indonesia), clove (*Syzygium aromaticum*, Greece), and nutmeg (*Myristica fragrans*, Indonesia) were pulverized using a blender (Rohnson, Heavy duty, Republic of Korea) to obtain the green coffee, cinnamon clove (1:1, w/w), and nutmeg powders used in the study. The materials were purchased from a local products shop in Agrinio (Aitolokarnania, Greece).

Chemicals and reagents

2,2-Diphenyl-1-picrylhydrazyl (DPPH[•]) was purchased from Sigma-Aldrich (Germany). Absolute ethanol (CH₃CH₂OH), sodium carbonate (Na₂CO₃), and acetate buffer (CH₃COONa × 3H₂O) were purchased from Merck (Darmstadt, Germany). Folin Ciocalteu reagent was purchased from Sigma-Aldrich. Gallic acid (3,4,5-trihydroxybenzoic acid) 99% isolated from *Rhus chinensis* Mill. was purchased from JNK Tech. Co. (Republic of Korea).

Quercetin [2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-chromen-4-one] (hydrate) was purchased from Cayman Chemical Company (Michigan, USA). Caffeic acid [3-(3,4-Dihydroxyphenyl)-2-propenoic acid] 98% was purchased from BLDpharm (Kaiserslautern, Germany).

Extraction of phytochemical compounds

Dry white wine (Grivas Winery, Agrinio, Aitolokarnania, Greece) was subjected to simple distillation to obtain ethanol of grape origin. Approximately, 200 mL of wine were transferred in flasks of 250 mL volume. Prior the distillation, there were added some glass stones (3–5) inside the flask avoid any sharp heating hearths. The distillation stopped when ca. 133 mL of ethanol were obtained in each case. The alcohol volume was 14.4% and was measured using an alcoholmeter (GECO, Germany). Then, 5 g of each powder was diluted with 50 mL of ethanol of grape origin in a plastic tube and the extracts were vortexed for 5 min. Finally, these were remained for 24 h in a dark place at room temperature for complete extraction. The next day the extracts were filtered with a filter paper and used for the analyses.

Determination of pH and color

For the determination of pH, 20 mL of the ethanolic extracts (10%, w/v) were transferred in a beaker and a portable pH-meter (*pHEP+*, HANNA Instruments, HI9808, Greece) was immersed in the solution. Results were expressed as pH units at 20 °C. In addition, for the determination of color characteristics such as blue color tone (BCT, OD₅₂₀), yellow color tone (YCT, OD₄₂₀), and red color tone (RCT, OD₆₂₀), the optical density (OD) at 420 nm, 520 nm, and 620 nm were measured using a SHIMADJU UV/VIS spectrophotometer (UV-1900, Kyoto, Japan).

$$\text{Color intensity : CI} = \text{OD}_{420} + \text{OD}_{520} + \text{OD}_{620}, \quad (1)$$

and

$$\text{color tone : } \text{OD}_{420}/\text{OD}_{520}, \quad (2)$$

were calculated by the measured color tones.

The contribution of colored pigments was also estimated by calculating the percent of yellow, red, and blue tones according to Ribéreau-Gayon et al. [17]:

$$\% \text{YCT}_{420} = (\text{OD}_{420})/(\text{CI}) \times 100, \quad (3)$$

$$\% \text{BCT}_{520} = (\text{OD}_{520})/(\text{CI}) \times 100, \quad (4)$$

$$\% \text{RCT}_{620} = (\text{OD}_{620})/(\text{CI}) \times 100, \quad (5)$$

Results were expressed as absorbance units (AU).

Determination of in vitro antioxidant activity of green coffee, cinnamon clove and nutmeg EEGO

Preparation of DPPH free radical standard solution (DPPH)

A standard solution of DPPH[•] equal to 1.34×10^{-4} mol/L (M), was prepared by dissolving 0.0053 g in 100 mL of absolute ethanol. The volumetric flask was wrapped with foil and stirred in a vortex apparatus. The obtained solution (pH = 7.02 ± 0.01) had a deep purple color and was left in the refrigerator for 2 h to stabilize.

Preparation of DPPH[•] calibration curve

A calibration curve of concentration versus absorbance of DPPH[•] was prepared as follows: The 1.34×10^{-4} M solution of DPPH was diluted with the addition of absolute ethanol. The obtained solutions were vortexed, left in the dark (until measurements were made), and their absorbance was measured at $\lambda_{\text{max}} = 517$ nm using the UV/VIS spectrophotometer mentioned above. The calibration curve of absorbance (*y*) versus concentration (*x*) of DPPH[•] was expressed by the following equation:

$$y = 0.0347x + 0.0652; R^2 = 0.9982 \quad (6)$$

Antioxidant activity parameters such as the %decrease in DPPH[•] absorbance (% antioxidant activity, %AA), % decrease in DPPH[•] concentration, % DPPH[•] remaining after the addition of the green coffee, cinnamon clove, and nutmeg EEGO to the DPPH[•] at the point where the reaction reached plateau, were estimated using the above calibration curve.

Determination of in vitro antioxidant activity

The antioxidant activity of green coffee, cinnamon clove, and nutmeg ethanolic EEGO was estimated in vitro according to the method of Karabagias et al. [18], with some modifications. The antioxidant activity was calculated using the following equation:

$$\% \text{AA} = (A_0 - A_t)/(A_0) \times 100\%, \quad (7)$$

Where A_0 is the initial absorbance of the DPPH[•] solution and A_t is the absorbance of remaining DPPH[•] after reaction with the antioxidants of green coffee, cinnamon clove, and nutmeg EEGO, at steady state (*t*, plateau).

For the test, volumes of 1.9 mL of absolute ethanol solution of DPPH[•] (1.34×10^{-4} mol/L) and 1 mL of acetate buffer

100 mmol/L (100 Mm) ($\text{pH}=7.10 \pm 0.01$) were placed in a cuvette, and the absorbance of the DPPH \cdot was measured at $t=0$ (A_0).

Subsequently, 0.1 mL of each EEGO studied, was added to the above medium and the absorbance was measured at regular time periods, until the absorbance value reached a plateau (steady state, A_t). The reaction in all cases was completed in 30 min. Each sample was measured in triplicate ($n=3$). For this antioxidant test ethanol and acetate buffer (2:1, v/v) were used as the blank sample.

Determination of effective concentration (EC_{50})

The effective concentration (EC_{50}) of the EEGO required to decrease the DPPH \cdot concentration by 50%, was estimated from graphs of the % DPPH \cdot remaining concentration versus different concentrations of green coffee, cinnamon clove, and nutmeg EEGO after proper dilutions equal to 2%, 4%, 6%, and 8% of the initial mother solution (10%, w/v). It should be stressed, that inhibition in DPPH \cdot concentration of the initial solution (10%, w/v), in each case (green coffee, cinnamon clove, and nutmeg EEGO), was also considered to obtain the EC_{50} values from calibration curves. The respective calibration curves were:

$$\text{Green coffee : } y = -67.871x + 58.129; R^2 = 0.991, \quad (8)$$

$$\text{Cinnamon clove : } y = -287.69x + 72.758; R^2 = 0.880 \quad (9)$$

$$\text{Nutmeg : } y = -57.099x + 62.29; R^2 = 0.979 \quad (10)$$

Determination of total phenolic content

The total phenolic content of green coffee, cinnamon clove, and nutmeg EEGO was determined using the Folin-Ciocalteu colorimetric method [18]. In particular, in a 5 mL volumetric flask, 0.20 mL of the ethanolic extracts of grape origin followed by 2.50 mL of distilled water and 0.25 mL Folin-Ciocalteu reagent were added. After 3 min, 0.50 mL of saturated sodium carbonate (Na_2CO_3 , 30% w/v) were also added into the mixture. Finally, the obtained solution was brought to 5 mL with distilled water. This solution was left for 2 h in the dark at room temperature and the absorbance was measured at $\lambda=760$ nm (after filtration with Whatman PES membrane filters) using the UV/VIS spectrophotometer mentioned before.

A calibration curve using gallic acid (GA) was prepared between 50–1500 mg/L:

$$y = 0.0041x + 0.39, R^2 = 0.9856 \quad (11)$$

Results were expressed as mg of gallic acid equivalents per liter (mg GAE/L) based on the calibration curve. Each sample was analyzed in triplicate ($n=3$).

Determination of caffeic acid content

The caffeic acid content of green coffee, cinnamon clove, and nutmeg EEGO were determined using a method developed in our laboratory. The filtered samples of 3 mL volume were introduced in a cuvette and the absorbance was measured at $\lambda=325$ nm considering the study of Bors et al. [19]. A calibration curve within the range of 0–11 mg/L was prepared by proper dilutions of the standard compound (initial concentration of 22 mg/L):

$$y = 0.1459x + 0.2046; R^2 = 0.9992 \quad (12)$$

Results were expressed as mg/L based on the calibration curve. Each sample was analyzed in triplicate ($n=3$).

Determination of quercetin content

The quercetin content of green coffee, cinnamon clove, and nutmeg EEGO were determined using a method developed in our laboratory. The filtered samples of 3 mL volume were introduced in a cuvette and the absorbance was measured at $\lambda=376$ nm (after scanning to get the maximum absorption in the UV/VIS spectrophotometer). A calibration curve within the range of 0–20 mg/L was prepared by proper dilutions of the standard compound (initial concentration of 20 mg/L):

$$y = 0.0623x + 0.1205; R^2 = 0.998 \quad (13)$$

Results were expressed as mg/L based on the calibration curve. Each sample was analyzed in triplicate ($n=3$).

Determination of volatile compounds

The volatile compounds of green coffee, cinnamon, clove, cinnamon clove, and nutmeg powders were determined using solid phase dynamic extraction coupled to gas chromatography/mass spectrometry (SPDE/GC–MS).

Extraction of volatile compounds

The NCT-SPNDL-01/AC-50-74 SPDE Needle 74 mm, 50 μm PDMS/AC coated fiber (BGB Analytik, Germany) was used for the extraction of the volatile compounds of green coffee, cinnamon clove, and nutmeg powders. The samples (ca. 1 g), were placed in screw-cap vials of 20 mL volume, equipped with PTFE/silicone septa. For the solid phase dynamic extraction, the vials were inserted in the chamber of the autosampler at 45 °C (incubation temperature). The pre-incubation time was 3 min., and the

conditioning time was 5 min. The syringe temperature was 35 °C. During the analysis of consecutive samples, 1 min delay was computed between samples to avoid any contamination.

Instrumentation and conditions of analysis

A Thermo Scientific gas chromatograph (TRACE GC Ultra) coupled to an DSQ II mass spectrometer was used for the analysis of the volatile compounds of green coffee, cinnamon, clove, cinnamon clove, and nutmeg powders. An Agilent DB-624 UI capillary column (20 m × 0.18 mm i.d., × 1 µm film thickness) was used, with helium as the carrier gas. For the analysis, the oven temperature was held at 40 °C for 5 min, increased to 90 °C at a rate of 15 °C/min (0 min hold), and finally increased to 220 °C at a rate of 30 °C/min (3 min hold). The oven temperature was 250 °C. The temperature of the ion source was 200 °C and the analysis was carried out on the positive mode within the mass range 45–260. Each sample was run in duplicate ($n=2$).

Identification of volatile compounds

The identification of volatile compounds was achieved using the NIST MS Search 2.0 (2002–2007) mass spectral library by considering the GC–MS spectra. The results were expressed as the relative percentage of each compound peak area to the sum of the identified GC–MS peak area:

$$\%VC \text{ (Volatile compounds)} = \frac{\text{Area of the identified compound}}{\text{Total area}} \times 100 \quad (14)$$

Statistical analysis

The collected data (phytochemical) concerning green coffee, cinnamon clove and nutmeg EEGO and data concerning volatile compounds of the raw powders (green coffee, cinnamon, clove, and nutmeg) were subjected to multivariate analysis of variance (MANOVA) to investigate the impact of the botanical origin of the tested materials on their phytochemical and volatile composition. Comparison of the average values of data was done using MANOVA at the confidence level $p < 0.05$. For the multivariate hypothesis, MANOVA creates a new dependent variable based on the linear combination of all the dependent variables inserted in the model (i.e., phytochemical data or volatile compounds), which maximizes as far as possible the differences in the average values between the level groups of the independent variable (i.e., green coffee, cinnamon clove, nutmeg EEGO). The Wilks' Lambda and Pillai's Trace criteria were implemented to study the main effects and interaction of the independent variables

at the multidimensional level [20]. The effectiveness of the used sample size in the experiment was estimated by the observed power. Power is the probability of rejecting the hypothesis that the means are equal when they are in fact not equal. The power during MANOVA depends on the sample size, the magnitudes of the variances, the alpha level, and the actual difference(s) among the population means in each group of objects. Therefore, high power is much desirable. The high power practically that there is a high probability of rejecting the null hypothesis when the null hypothesis is false. This is a critical measure of precision in hypothesis testing during the application of multivariate statistics [21].

Factor analysis (FA), as a dimension reduction technique (unsupervised statistical technique), describes the variability (variance) that exists between an initial number of measured (obvious) and associated variables, and a smaller number of non-obvious variables, called factors. The purpose of factor analysis is to summarize the relationships between the initial and the factor variables in a comprehensive and accurate way by providing percentages of variance (% variance) associated with those factors. The extraction method was PCA with Varimax rotation and Keiser Normalization [22]. Pearson's correlation bivariate statistics ($-1 \leq r \leq +1$) was also carried out at the confidence level $p < 0.05$. Statistical analysis was done using the Statistical Package for the Social Sciences (SPSS) version 28.0 statistics software (SPSS, IBM Inc., 2021).

Results and discussion

Phytochemical composition of green coffee, cinnamon clove, and nutmeg EEGO

MANOVA showed that there were statistically significant differences on the phytochemical composition of green coffee, cinnamon clove, and nutmeg ethanolic extracts as shown by Pillai's trace (Value = 2.000, $F = 2,686,828,713$, $p < 0.001$) and Wilks' lambda (Value = 0.000, $F = 3.157 \times 10^{12}$, $p < 0.001$) indices. In addition, the observed power in both cases was 1.000. Table 1 shows the summarized data along with their statistical evaluation criteria.

The pH of spices, herbs and coffee is a mandatory quality criterion. More specifically, coffee has a wide range of acids in its composition. Among them, acetic, citric, chlorogenic, malic and quinic acids are the most abundant in coffee. The acid content in the composition of coffee depends on numerous factors, such as the altitude of the place of cultivation, ripeness of the beans, roasting, and occurrence of fermentation during the drying process. In this context, the pH value can be indicative of changes in coffee beans,

Table 1 Physicochemical parameter values and phytochemical content of green coffee, cinnamon clove, and nutmeg EEGO

EEGO	pH	AA (%)	EC ₅₀ (mg/L)	TPC (mg GAE/L)	Caffeic acid (mg/L)	Quercetin (mg/L)	OD ₄₂₀	OD ₃₂₀	OD ₆₂₀	%YellowCT	%BlueCT	%RedCT
Green coffee	5.24±0.02 ^a	59.62±0.01 ^d	0.11±0.01 ^e	1160.49±0.01 ^j	1978.20±0.01 ^m	141.75±0.01 ^p	2.35±0.07 ^s	1.76±0.06 ^v	1.44±0.06 ^z	42.35±0.01 ^{ab}	31.67±0.01 ^{ac}	25.98±0.01 ^{ab}
Cinnamon clove	4.20±0.01 ^b	55.12±0.01 ^e	0.08±0.01 ^h	1120.24±0.01 ^k	634.65±0.01 ⁿ	566.77±0.01 ^q	11.23±0.08 ^t	2.03±0.04 ^w	0.86±0.08 ^z	79.47±0.01 ^{ac}	36.67±0.01 ^{af}	6.12±0.01 ^{ai}
Nutmeg	4.99±0.01 ^c	57.24±0.01 ^f	0.21±0.01 ⁱ	199.39±0.01 ^l	30.43±0.01 ^o	18.23±0.01 ^r	0.59±0.02 ^u	0.36±0.01 ^x	0.29±0.02 ^{aa}	47.98±0.01 ^{ad}	28.76±0.40 ^{ag}	23.02±0.01 ^{aj}
F	61.50*10 ²	15.20*10 ⁵	44.61*10 ¹	88.66*10 ⁸	29.82*10 ⁹	44.97*10 ¹	24.84*10 ⁸	32.37*10 ¹	12.87*10 ²	92.04*10 ¹	12.01*10 ⁶	34.44*10 ⁵
p	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

F Values of the F-function, p probability-significance. Different letters in each column indicate statistically significant differences ($p < 0.05$). Each sample was analyzed in triplicate ($n = 3$)

such as undesirable fermentations that can occur before or after harvesting [10].

The highest pH value (5.24 ± 0.02) was recorded for green coffee, followed by nutmeg (4.99 ± 0.01), and cinnamon clove (4.20 ± 0.01) EEGO.

In a previous study, the pH of Brazilian green coffee (*Coffea arabica* L.) ranged between 5.70 and 5.84, with an average of 5.78 ± 0.02 [10], in agreement with the results of the present study. Cinnamon and clove used as essential oils in different proportions, to improve physical, thermal, and antimicrobial properties of chitosan-gum arabic polyelectrolyte complexed films, had pH values ranging between 4.29 ± 0.01 to 4.32 ± 0.01 for cinnamon essential oil and 4.31 ± 0.01 for clove essential oil [23]. These pH values are in agreement with the results of the present study.

The antioxidant activity (percent inhibition of the DPPH) varied significantly ($p < 0.05$) with respect to the studied EEGO. The highest AA value ($59.62 \pm 0.01\%$) was recorded for green coffee, followed by nutmeg ($57.24 \pm 0.01\%$), and cinnamon clove ($55.12 \pm 0.01\%$) EEGO, respectively. The EC₅₀ followed the respective order: nutmeg (0.214 ± 0.001 mg/L) > green coffee (0.110 ± 0.01 mg/L) > cinnamon clove (0.078 ± 0.001 mg/L) EEGO. It has been reported previously, that coffee has a high antioxidant activity and has been proposed to be the major natural source of antioxidants [24]. We should not forget that antioxidants are essential for a considerable number of bioactivities in the human body, preventing thus, the oxidation of other molecules in our body. The total antioxidant content of coffee has been reported to be approximately 0.15–0.30 mg/g [25]. In a recent study, the antioxidant activity of green coffee from Ethiopia reached 70.32% [12].

On the other hand, cinnamon, clove, and nutmeg possess antioxidant activity due to the presence of numerous terpenoids and phenolic compounds including β -caryophyllene, α -pinene, camphene, eugenol, cinnamaldehyde, etc., having hydrogen atoms in the allylic or benzylic positions [1]. Given the comparatively simple abstraction of atomic hydrogen from these functional groups, these compounds have high antioxidant activity. The abstraction of atomic hydrogen is done by peroxy-radicals that are produced under oxidative stress. In addition, the role of eugenol in nutmeg favors the antioxidant activity by promoting the activities of specific enzymes, such as superoxide dismutase, catalase, glucose-6-phosphate dehydrogenase, glutathione peroxidase and glutamine transferase [7].

Total phenolic content, caffeic acid and quercetin contents varied significantly ($p < 0.05$) with respect to green coffee, cinnamon clove, and nutmeg EEGO (Table 1). Among the studied EEGO, green coffee recorded the highest total phenolic and caffeic acid content (1160.49 ± 0.01 mg GAE/L and 1978.20 ± 0.01 mg/L, respectively) followed by cinnamon clove (1120.24 ± 0.01 mg GAE/L and

634.65 ± 0.01 mg/L, respectively) and nutmeg (199.39 ± 0.01 and 30.43 ± 0.01, respectively). However, quercetin recorded the highest content in cinnamon clove (566.77 ± 0.01 mg/L), followed by green coffee (141.75 ± 0.01 mg/L) and nutmeg (18.23 ± 0.01 mg/L) EEGO, respectively. Among the compounds with antioxidant activity, phenolic compounds represent the major compounds of the antioxidant activity of coffee. Some potential biochemical compounds comprise caffeine, chlorogenic acid (CGA), sucrose and trigonelline, which have been used for the characterization of coffee species. CGA is the most prevalent phenolic compound in coffee [12]. Other phytochemicals of cinnamon and clove include eugenol (or acetyl eugenol), beta-caryophyllene, vanillin, crategolic acid, tannins, such as bicornin [26, 27] gallotannic acid, methyl salicylate, eugenin, kaempferol, rhamnetin, and eugenitin, triterpenoids such as oleanolic acid, stigmasterol, and campesterol along with several sesquiterpenes [28]. Nutmeg has been reported also to be a rich source of phenylpropanes such as myricitin, safrole, and elmicin [29]. There was a positive and significant correlation between antioxidant activity and caffeic acid content ($r = 0.698$, $p = 0.037$), and between total phenolic content with caffeic acid content ($r = 0.763$, $p = 0.017$), with respect to the green coffee, cinnamon clove, and nutmeg EEGO. A negative and significant correlation was monitored between antioxidant activity and quercetin content ($r = -0.716$, $p = 0.030$) among the studied EEGO.

The color parameters (color intensity, OD₄₂₀, OD₅₂₀, OD₆₂₀, %YellowCT, %BlueCT, and %RedCT) differed significantly ($p < 0.05$) with respect to green coffee, cinnamon clove, and nutmeg EEGO (Table 1). The OD₄₂₀ recorded the highest value in cinnamon clove (11.23 ± 0.80 AU) followed by green coffee (2.35 ± 0.07 AU), and nutmeg (0.59 ± 0.01 AU) EEGO, respectively. Similarly, the OD₅₂₀ recorded the highest value in cinnamon clove (2.03 ± 0.04 AU), followed by green coffee (1.76 ± 0.06 AU), and nutmeg (0.36 ± 0.01 AU) EEGO, respectively. On the other hand, the OD₆₂₀ recorded the highest value in green coffee (1.44 ± 0.06 AU), followed by cinnamon clove (0.86 ± 0.08 AU), and nutmeg (0.29 ± 0.01 AU) EEGO, respectively.

The %Yellow CT recorded the highest value in cinnamon clove (79.47 ± 0.01%), followed by nutmeg (47.98 ± 0.01%), and green coffee (42.35 ± 0.01%) EEGO, respectively. Similarly, the %Blue CT recorded the highest value in cinnamon clove (36.67 ± 0.01%), followed by green coffee (31.67 ± 0.01%), and nutmeg (28.76 ± 0.40%) EEGO, respectively. Finally, the %Red CT recorded the highest value in green coffee (25.98 ± 0.01%), followed by nutmeg (23.02 ± 0.01%), and cinnamon clove (6.12 ± 0.01%) EEGO, respectively. Colour of natural food sources or their extracts is closely associated with pigments (carotenoids and polyphenols) [18] and comprises a major qualitative criterion by consumers [1].

FA also showed that were potential factors that could be associated with the variance explained by the measured parameters. More specifically, there were 2 principal components (PCs) that explained 99.833% of the total variance. These components were %YellowCT (PC1) with eigenvalue equal to 7.797, correlation of 0.999, and 58.944% contribution to the total variance, and OD₆₂₀ (PC2) with eigenvalue equal to 4.183, correlation of 0.980, and 40.889% contribution to the total variance. Figure 1 shows the allocation of the measured parameters (components) to the rotated space of FA.

Volatile compounds of green coffee, cinnamon clove, cinnamon clove, and nutmeg powders

Volatile compounds with a high NIST mass spectral library probability level

Twelve volatile compounds were identified with probability level > 80% according to the NIST mass spectral library, among the analyzed samples (Table 2). It's worth noting that these compounds belong to different classes such as hydrocarbons, nitrites, acids, esters, aldehydes, ketones, terpenoids, and phenolic compounds. The volatile composition (%) differed significantly ($p < 0.05$) with respect to green coffee, clove, cinnamon, cinnamon clove, and nutmeg powders as shown by MANOVA (Pillai's Trace: Value = 1.995, $F = 721.019$, $p < 0.001$ and Wilks' Lambda: Value = 0.000, $F = 444,310.624$, $p < 0.001$). Figure 2 shows a representative gas chromatogram of cinnamon clove powder indicating the identified volatile compounds.

Green coffee powder had the richest aroma (78.37%), as sum of the individual volatile compounds, followed by nutmeg (3.27%), and cinnamon clove (2.60%) powders.

Among the identified volatile compounds, some possess some special characteristics and properties. Sec-butyl nitrite comprises an alkyl nitrite. Food sources of nitrites include vegetables, fruit, and processed meats. In addition, nitrites are produced endogenously through the oxidation of nitric oxide and through a reduction of nitrate by commensal bacteria in the mouth and gastrointestinal tract. As such, the dietary provision of nitrates and nitrites from vegetables and fruit may contribute to the blood pressure-lowering effects of the dietary approaches to stop hypertension (DASH) diet [30].

Ethyl acetate occurs in several natural products and contributes to the characteristic aroma of many fruits and wine. Ethyl acetate is also found in varying concentrations in foodstuffs, including green and roasted coffee. In the decaffeination process the combination of water and ethyl acetate is used [31]. Ethyl acetate was identified in the highest

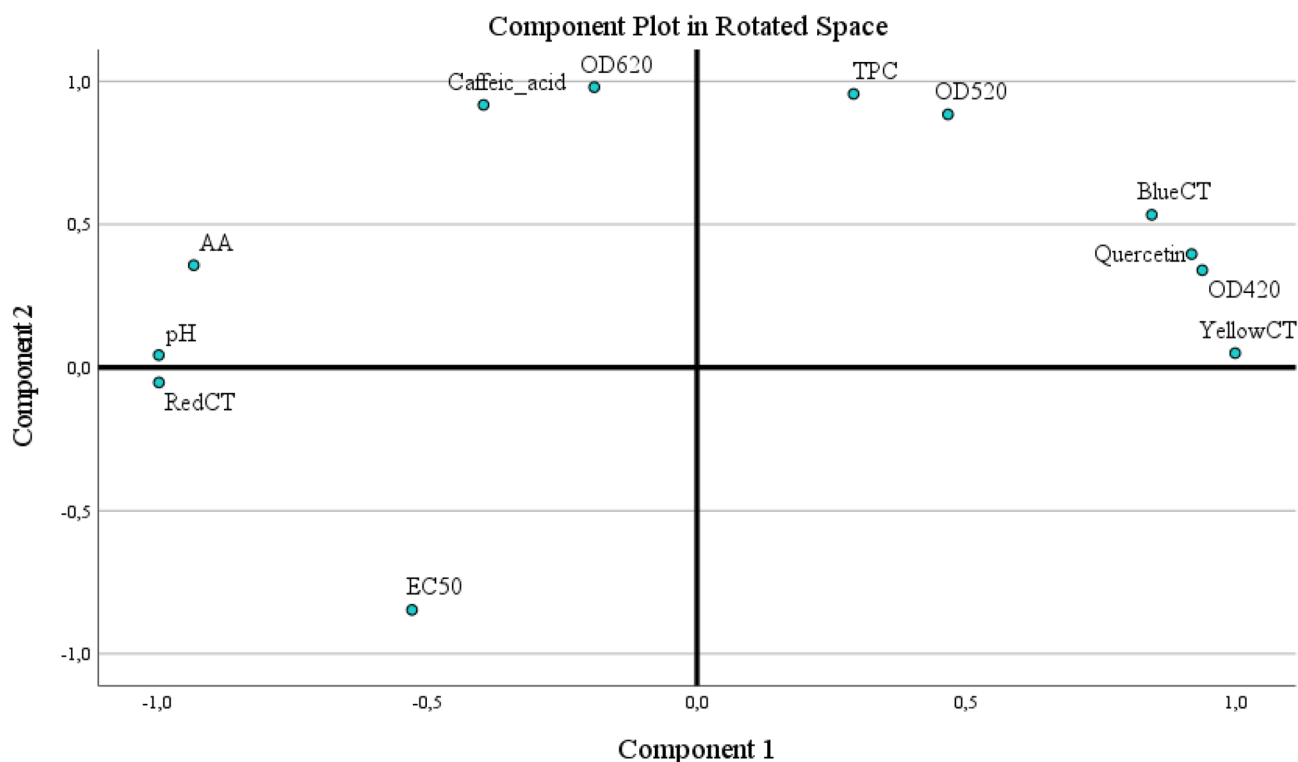


Fig. 1 Allocation of physicochemical and phytochemical parameters (components) of green coffee, cinnamon clove, and nutmeg EEGO to the 2D-rotated space of FA

proportion ($5.75 \pm 0.02\%$) in green coffee followed by nutmeg powders ($0.18 \pm 0.18\%$).

Methyl salicylate is the methyl ester of salicylic acid. It has a sweet, fruity odor reminiscent of root beer, but often is characterized as "minty", as it comprises an ingredient in mint candies [32]. Methyl salicylate was identified only in cinnamon clove ($0.74 \pm 0.04\%$) powder. The present findings are in agreement with those of Bhuiyan et al. [14], who reported the presence of methyl salicylate in the essential oil of clove leaves from Bangladesh. It is then possible, that methyl salicylate may comprise a potential volatile compound of cinnamon/clove found either in powder or in essential oil form. The same holds for 2-nonanone (Table 2), a ketone that has been associated with fruity and cheesy flavor (The Good Scents Company, 2019).

Vitamin A aldehyde, commonly known as retinal or retinaldehyde is among the chemically related organic compounds that refer to Vitamin A (retinol, retinoic acid, beta-carotene) and have biological activities [33]. Retinal was identified in the highest proportion in green coffee ($0.25 \pm 0.17\%$), followed by cinnamon clove ($0.015 \pm 0.005\%$) powders.

Para-pentyl acetophenone was identified only in green coffee powder, whereas 2-nonanone in cinnamon clove powder (Table 2). The presence of ketones in roasted green

coffee [34] or in spices [14, 16] has been reported previously, in agreement with the results of the present study.

Finally, terpinen-4-ol was identified only in nutmeg ($1.46 \pm 0.41\%$) powder. Terpin-4-ol has been associated with a musty odor [32]. In a previous study, terpinene-4-ol was identified in small proportions (0.4%) in the essential oil of the leaves of clove from Bangladesh [14].

Similar to phytochemical/physicochemical parameter analyses, FA also showed that were potential volatile compounds (factors) that could be associated with the variance explained by the identified volatile compounds. More specifically, there were 2 principal components (PCs) that explained 95.919% of the total variance. These components were sec-butyl nitrite (PC1) with eigenvalue equal to 7.768, correlation of 0.990, and 63.024% contribution to the total variance, and methyl salicylate (PC2) with eigenvalue equal to 3.743, correlation of 0.912, and 32.895% contribution to the total variance. Figure 3 shows the distribution of the volatile compounds (components) to the rotated space of FA.

Volatile compounds with a lower NIST mass spectral library probability level

Fourteen volatile compounds were also identified in a lower probability level according to NIST mass spectral

Table 2 Volatile compounds of green coffee, cinnamon clove, and nutmeg powders with a high probability level

RT	Volatile compounds	RI*	Green coffee (Avg ± SD)	Cinnamon clove (Avg ± SD)	Nutmeg (Avg ± SD)	F	P	Probability (%) in green coffee	Probability (%) Cinnamon clove	Probability % Nutmeg	
	<i>Alcohols</i>										
1.05	Methyl alcohol	381	5.19 ± 0.33	4.19 ± 0.39	0.83 ± 0.20	47.29*10 ¹	<0.001	92.13	90.05	91.76	
	<i>Aldehydes</i>										
14.14	Vitamin A aldehyde (Retinal)	–	0.25 ± 0.17	0.02 ± 0.01	ni	6.117	0.036	95.84	85.18	–	
	<i>Alkyl nitrites</i>										
6.47	sec-Butyl nitrite	542	0.06 ± 0.02	ni	ni	40.333	<0.001	83.09	–	–	
	<i>Hydrocarbons</i>										
0.68	Ethylene	165	49.78 ± 0.02	ni	ni	18.585*10 ⁶	<0.001	93.06	–	–	
2.46	3-Methylpentane	589	25.41 ± 0.03	ni	0.76 ± 0.75	33.84*10 ²	<0.001	86.15	–	84.34	
8.71	2-Chloro-2-nitro- propane	–	0.71 ± 0.02	0.06 ± 0.00	0.05 ± 0.04	64.37*10 ¹	<0.001	86.94	85.23	87.39	
	<i>Esters</i>										
1.89	Methyl acetate	516	ni	0.27 ± 0.06	ni	69.645	<0.001	–	91.06	–	
3.41	Ethyl acetate	601	5.75 ± 0.02	ni	0.18 ± 0.17	31.027*10 ²	<0.001	95.93	–	95.29	
12.67	Methyl salicylate	1185	ni	0.735 ± 0.04	ni	13.23*10 ²	<0.001	–	86.15	–	
	<i>Ketones</i>										
11.90	2-Nonanone	1096	ni	1.26 ± 0.09	ni	18.75*10 ²	<0.001	–	88.04	–	
12.75	p-Pentylacetophe- none	–	0.24 ± 0.12	ni	ni	12.527	0.007	90.10	–	–	
	<i>Terpenoids</i>										
12.51	3-Cyclohexen-1-ol, 4-methyl-1-(1- methylethyl) (Terpinen-4-ol)	1179	ni	ni	1.46 ± 0.41	38.042	<0.001	–	–	98.63	

RT Retention time (minutes), F Values of the F-function, p probability-significance, Avg average value, SD standard deviation, ni not identified, were treated as zero for chemometrics, RI* Retention time indices (Kovats indices) according to NIST [41], considering the similar capillary column characteristics used in the present study. Each sample was analyzed in duplicate (n = 2)

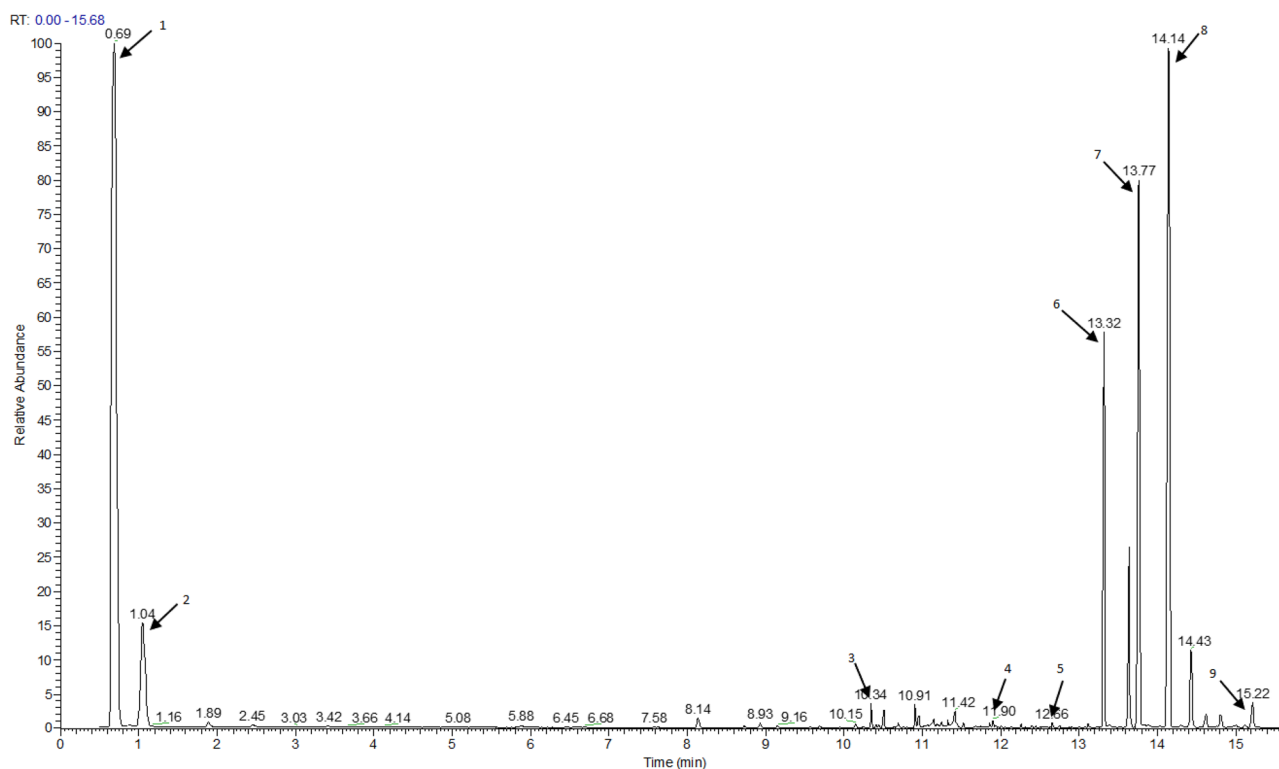


Fig. 2 A representative gas chromatogram of cinnamon clove powder. 1: Ethylene. 2: Methyl alcohol. 3: 2-Heptanone. 4: 2-Nonanone. 5: Methyl salicylate. 6: 1,3 dihydro, 2H-Inden-2-One. 7: Eugenol. 8: Vitamin A aldehyde (Retinal). 9: Phenol, 2-methoxy-4-(2-propenyl), acetate

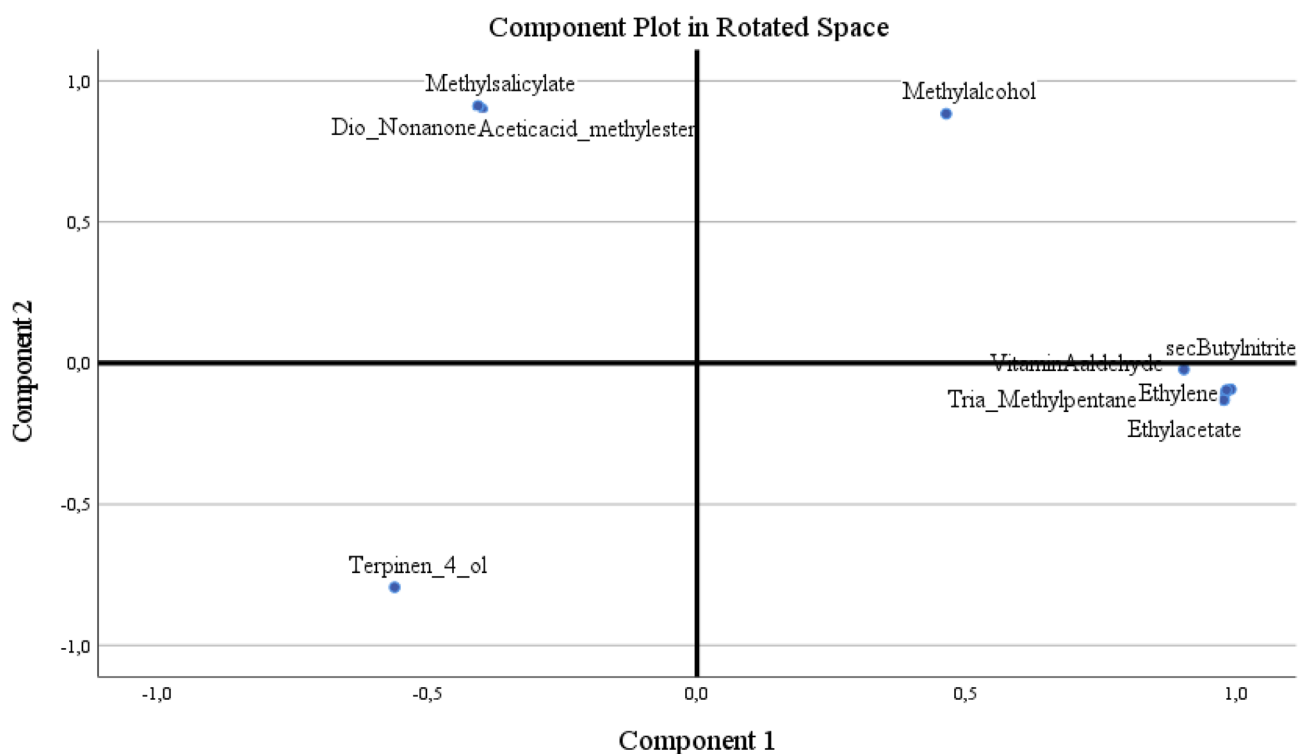


Fig. 3 Allocation of the most probable volatile compounds (components) of green coffee, cinnamon clove, and nutmeg powders to the 2D-rotated space of FA

library. MANOVA showed significant differences based on the volatile composition of green coffee, cinnamon clove, and nutmeg powders (Pillai's Trace: Value = 1.998, $F = 1515.418$, $p < 0.001$ and Wilks' Lambda: Value = 0.000, $F = 2668.279$, $p < 0.001$). Among these volatile compounds, 12 showed statistically significant differences in their % percent proportion with respect to green coffee, cinnamon clove, and nutmeg powders (Table 3).

The most characteristic volatile compound was eugenol. Eugenol comprises an allyl-benzene, and was identified in the highest proportion in cinnamon clove ($14.03 \pm 0.15\%$), followed by green coffee powders ($1.19 \pm 0.09\%$). It has been associated with a pleasant, spicy, and clove-like scent, and has been extracted from essential oils, especially from clove, nutmeg, cinnamon, basil and bay leaf [14]. The same holds for estragole, a phenylpropene, which was identified only in cinnamon clove powder ($0.08 \pm 0.01\%$). It is a component of various trees and plants, including turpentine (pine oil), anise, fennel, bay, tarragon, and basil [35]. In addition, in a

previous study estragole was identified in commercial white pepper samples from the Netherlands market. Estragole has been associated with a sweet licorice flavor [16].

Bhuiyan et al. [14] reported that the essential oil obtained by hydro-distillation from fresh leaves and dry buds of clove (*Syzygium caryophyllatum*) had important proportions of eugenol (74.3%), followed by eucalyptol (5.8%), caryophyllene (3.85%), and α -cadinol (2.43%). The main components in bud oil were also eugenol (49.7%), caryophyllene (18.9%), benzene,1-ethyl-3-nitro (11.1%) and benzoic acid,3-(1-methylethyl) (8.9%). Results of the present study, concerning mainly eugenol, are in agreement with those of Bhuiyan et al. [14]. However, the authors did not mention the probability level of each of the identified compound.

The volatile compound 9-hexadecen-1-ol was identified in the highest proportions in green coffee ($0.13 \pm 0.01\%$), followed by cinnamon clove ($0.05 \pm 0.00\%$) powders, whereas 9-tetradecen-1-ol was identified only in nutmeg powder ($0.21 \pm 0.17\%$). It should be stressed, that 9-hexadecen-1-ol

Table 3 Volatile compounds of green coffee, cinnamon clove, and nutmeg powders with a lower probability level

RT	Volatile compounds	Green coffee (Avg \pm SD)	Cinnamon clove (Avg \pm SD)	Nutmeg (Avg \pm SD)	F	<i>p</i>	Propability (%) in green coffee	Propability (%) in cinnamon clove	Propability (%) in nutmeg
<i>Alcohols</i>									
5.32	9-Hexadecen-1-ol	0.13 ± 0.005	0.05 ± 0.00	ni	14.25×10^2	$<.001$	19.57	30.86	–
13.33	9-Tetradecen-1-ol	ni	ni	0.21 ± 0.17	4.631	0.061	–	–	53.00
<i>Hydrocarbons</i>									
10.94	Decane	0.94 ± 0.05	ni	ni	12.95×10^2	$<.001$	75.09	–	–
11.40	Undecane	0.91 ± 0.005	ni	ni	98.28×10^3	$<.001$	29.38	–	–
12.26	Dodecane	0.39 ± 0.02	0.06 ± 0.00	ni	99.23×10^1	$<.001$	51.41	53.66	–
<i>Ketones</i>									
10.34	2-Heptanone	ni	0.48 ± 0.03	ni	76.80×10^1	$<.001$	–	78.31	–
13.32	2H-Inden-2-One,1,3 dihydro	ni	7.30 ± 0.21	ni	36.25×10^2	$<.001$	–	55.12	–
<i>Phenolic compounds</i>									
13.11	Estragole	ni	0.08 ± 0.01	ni	19.20×10^1	$<.001$	–	57.30	–
13.74	Eugenol	1.19 ± 0.09	14.03 ± 0.15	ni	18.33×10^3	$<.001$	35.86	52.31	–
15.12	4-Methoxycinnamaldehyde	ni	ni	0.24 ± 0.19	4.787	0.057	–	–	28.16
15.22	Phenol, 2-methoxy-4-(1-propenyl)-, acetate	0.69 ± 0.18	1.13 ± 0.38	ni	16.662	0.004	68.34	42.64	–
<i>Terpenoids</i>									
10.50	α -Terpinolene	ni	0.30 ± 0.02	3.22 ± 0.63	71.808	$<.001$	–	55.12	69.73
11.16	α -Terpinene	ni	ni	2.89 ± 0.32	24.47×10^1	$<.001$	–	–	75.89
12.60	2-Carene	ni	ni	0.24 ± 0.18	5.41	0.045	–	–	28.90

RT: Retention time (minutes). F: Values of the F-function, *p*: probability-significance. Avg: average value, SD: standard deviation. ni: not identified; were treated as zero for chemometrics. Each sample was analyzed in duplicate (n = 2)

was identified previously contributing to the volatile profile of *Foeniculum vulgare* essential oil in higher proportions (1.97%) [36].

α -Terpinolene and α -terpinene were identified in higher proportions in nutmeg powder ($3.22 \pm 0.63\%$ and $2.89 \pm 0.32\%$, respectively). A significant ($p < 0.05$) lower proportion of α -terpinolene was identified in cinnamon clove powder ($0.30 \pm 0.02\%$), whereas in green coffee powder these were absent. Terpenoids are naturally present in herbs, spices or green coffee [1, 16, 34].

It is quite interesting the identification of 1,3-dihydro-2H-Inden-2-one in considerable proportions ($7.30 \pm 0.21\%$) only in cinnamon clove powder. This compound comprises a dehydrated indenone. Indenones have been reported to act as intermediates for the synthesis of other molecules [37]. The properties these compounds have might be of interest for the food and the drug sector.

2-Methoxy-4-(1-propenyl)-phenol acetate was identified in the highest proportion in cinnamon clove ($1.13 \pm 0.38\%$) followed by green coffee ($0.69 \pm 0.18\%$) powders. Phenolic compounds have been previously identified in the essential oil of clove leaves [14] and in green coffee from different countries (Brazil, Colombia, Costa Rica, Ethiopia, Guatemala, Honduras, India, Kenya, Mexico, Nicaragua, Rwanda, Uganda and Vietnam) [15]. However, 2-methoxycinnamaldehyde was identified only in nutmeg powder (Table 3). 2-Methoxy cinnamaldehyde comprises a bioactive component identified previously in *Agastache rugosa* (Korean mint or Chinese patchouli, etc.) [38].

Hydrocarbons such as decane, undecane, and dodecane were identified only in green coffee powder (Table 3). In a recent study, decane, undecane, and dodecane were identified in roasted green coffee from different countries (Brazil, Burundi, Colombia, Costa Rica, Democratic Republic of Congo, Dominican Republic, El Salvador, Ethiopia, Guatemala, Haiti, Honduras, India, Indonesia, Kenya, Peru, Republic of Panama, Rwanda, and Uganda) [34]. On the other hand, 2-carene was identified only in nutmeg powder (Table 3). Carene has been associated with sweet and pungent odor. It has been previously reported to contribute to the aroma of cannabis essential oil [39].

2-Heptanone was identified only in cinnamon clove powder (Table 3). It has been associated with a banana-like and fruity odor [40].

FA also indicated factors that could be associated with the variance explained by the identified volatile compounds. In particular, there were 3 principal components (PCs) that explained 98.847% of the total variance. These components were eugenol (PC1) with eigenvalue equal to 5.719, correlation of 0.969, and 40.849% contribution to the total variance, 9-hexadecen-1-ol (PC2) with eigenvalue equal to 5.148, correlation of 0.925, and 36.773% contribution to the total variance, and 9-tetradecen-1-ol (PC3) with eigenvalue equal to

Component Plot in Rotated Space

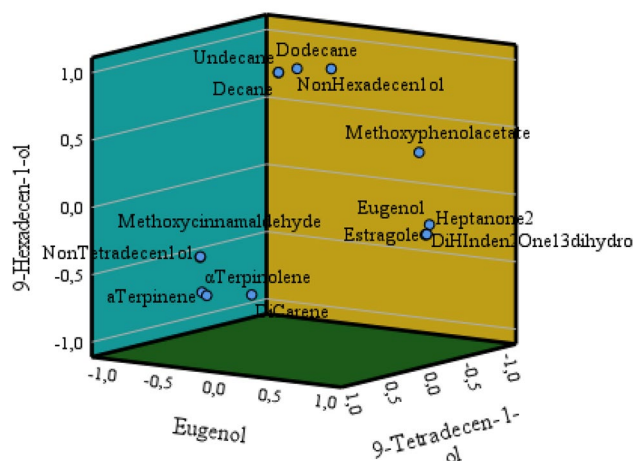


Fig. 4 Allocation of the less probable volatile compounds (components) of green coffee, cinnamon clove, and nutmeg powders to the 3D-rotated space of FA

2.971, correlation of 0.906, and 21.225% contribution to the total variance. Figure 4 shows the allocation of the volatile compounds (components) to the rotated space of FA.

Conclusions and future perspectives

Results of the present study showed that alcohol of grape origin collected after distillation of dry white wine can be an alternative solvent for the extraction of phytochemicals with high antioxidant activity from natural sources, such as green coffee, cinnamon clove, and nutmeg powders, which also possess a characteristic aroma owed to the presence of alcohols, aldehydes, hydrocarbons, ketones, terpenoids, phenolic compounds, etc. Given the continuous trend in the global zone for the support of circular economy with the reduction of plastics and chemicals, the present study, novel in nature as not previously reported, aids to this purpose. In this context, the EEGO of green coffee, cinnamon, clove, and other spices, can be an alternative option for food preservation, with an ‘‘eco- and human-friendly’’ character. Ongoing research from our group will further validate this hypothesis.

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Karabagias would like to dedicate this research work in beloved memory of his father Konstantinos.

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Data availability The manuscript includes all relevant data.

Declarations

Conflict of interest The authors declare that they have no conflict of interest or competing interests.

Compliance with ethics requirements This article does not contain any studies with human or animal subjects.

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